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Electrooxidation of Imidazole to Form Soluble Electroactive Polymer

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Over the past two decades, several polymers have been electrochemically prepared with conductivities up to 103 S cm <sup>-1</sup> . Here, we introduce imidazole (1 mz) monomer as an alternative starting material. Imz has been electrochemically oxidized at the anode of an electrochemical cell. Soluble, electroactive polymeric products of low molecular weight have been synthesized. The oxidation product, which has yet to be displayed as a free standing film, can be studied more thoroughly due to its solution ability. Reaction conditions are to be presented along with polarization curves and current vs. time plots. Product yield as a function of reaction time will be given. Characterization by elemental analysis and uvvis spectroscopy will also be presented. <span style="border: 1px solid black; padding: 2px;">17</span>			
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## Electrooxidation of Imidazole to Form Soluble Electroactive Polymer

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### Introduction

Imidazole possesses high polarity, a high degree of aromaticity and is similar in architecture to the pyrrole molecule.<sup>1-3</sup> When oxidized, polypyrrole conducts electrically with conductivities in the range of  $10^3$  to  $10^2$  S cm<sup>-1</sup>. Conductivity of polypyrrole is attributed to its delocalized electronic structure that is formed through pi bonding. It is well established that pyrrole can be reacted electrochemically via a radical cation mechanism in the presence of an anionic electrolyte, that serves as a dopant, to form the oxidized conducting form of polypyrrole.<sup>4</sup> It is speculated that imidazole could also be electropolymerized into a conductive or possibly a semiconductive film as well. Similar heteroazole containing polymers have been produced.<sup>5</sup>

Commonly known polymers of imidazole include both transition metal complexes and vinyl imidazole polymers. The areas of current use of imidazole polymers include catalysts, protein complexes with heme groups of transition metals, photographic dyes, photoconductive or other electroactive donor-acceptor complexes, and ion exchange membranes and resins.<sup>6,7</sup>

Very little has been published on the oxidation of imidazole, most probably due to the fact that the potential wave for imidazole is occluded by the solvent wave. Some work has been reported on the cyanation of 1-methylimidazoles by electrooxidation.<sup>8</sup>

### Results and Discussion

The electrochemical reactions were performed in a two compartment cell designed with a graphite rod cathode, an anode compartment that held a Pt plate and an SCE reference electrode. The cell was driven by a model 231 Princeton Applied Research potentiostat-galvanostat. Typically, a reaction vessel contained 75 mL of a 1 M solution of imidazole holding 0.25 M to 1 M electrolyte in deionized water. Proven electrolyte materials for this reaction included NaCl, NaClO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, and (CH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>NBF<sub>4</sub>, the latter having been reacted in acetonitrile solvent. Reactions were temperature regulated at 17 to 35 °C, with constant stirring. Reaction voltages, (held constant in each reaction), were also varied up to 2.75 volts vs. SCE, above which the oxidation of H<sub>2</sub>O was too excessive for the potentiostat to control.

Product formation is indicated by the coloration of the solution with reaction time. The solution is initially clear and colorless, but changes sequentially to yellow, amber, brown, and finally black-brown as product forms. Coloration is observed within the first 10 minutes of the

reaction and, at longer reaction times, a black powder forms along with a weak film at the electrode.

Figure 1 displays the drop in current over time for the oxidation of 1 M imidazole in 1 M NaCl reacted at a potential of 2.50 volts at 35 °C. The measured pH decreased considerably with increasing reaction time as noted at various stages of the reaction. Once the pH falls below about a value of 5, the solution fades to a clear, light brown color between 15 and 20 hours of reaction indicating the onset of a further chemical reaction. At a starting pH of about 6, product is formed very slowly. Reactions that were carried out in buffering solutions containing Na<sub>2</sub>HPO<sub>4</sub> as the electrolyte showed a higher yield of precipitating product.

Reaction temperature also plays a role in the ability to form an oxidation product as shown by reactions using 0.25 M Na<sub>2</sub>SO<sub>4</sub> as the electrolyte. The reaction was carried out at 2.50 volts at temperatures of 17, 20, 23, and 30 °C. Product formation occurred very slowly at 17 °C, but reactions proceeded much more rapidly at higher temperatures.

The oxidation products can be cleanly fractionated into a high molecular weight black solid precipitate and a low molecular weight clear brown solution by filtration through a 0.45 µm filter followed by subsequent washing. The black precipitate can be dissolved in a few organic solvents, including DMSO and a mixture of acetone and water having the same solubility parameter as DMSO. By contrast, polypyrrole is an insoluble, intractable polymer. Also, the precipitate dissolves in aqueous solutions containing either dilute acid or base, or surfactants such as sodium dodecylsulfate. Although solubility is limited, it appears to be independent of the supporting electrolyte. Following fractionation, the clear brown soluble portion can be dried and then dissolved in a wide range of polar organic solvents.

The total electrochemical product yield has not been determined. However, it is significantly greater than even the maximum yield of 5% determined from the insoluble precipitate in a 15 hour reaction that used Na<sub>2</sub>HPO<sub>4</sub> as the electrolyte. After 15 hours, the precipitate yield decreased dramatically.

The elemental analysis of the black precipitate from the NaCl reaction gives a stoichiometric ratio of 2.7:2.6:2.2:1.0 for C:H:N:O respectively. This ratio roughly retains the ratio of C:H:N for the imidazole monomer, with the addition of about one oxygen per repeat unit.

UV-vis spectra are shown in figure 2 for the imidazole monomer, the fractionated water soluble portion of the electrooxidized reaction, and the water insoluble precipitate of the same reaction, (all at  $4.34 \times 10^{-4}$  M), which had been run for 10 hours at 2.50 volts and 35 °C. This figure clearly demonstrates absorption at visible wavelengths. This supports the idea that new, larger chromophores are being created in the oligomeric and polymeric species formed during electrooxidation.

Figure 3 displays the spectral trends of the solid precipitate taken from the same reaction conditions as used in figure 2 after oxidations of 5, 10, 15, and 20 hours. It appears that the 5 hour sample contains the largest quantity of chromophores that absorb in the visible. The 10 and 15 hour samples contain even lower quantities of these chromophores, while the 20 hour sample contains the least. This trend, combined with the data on lower yields, suggests that a further, perhaps degradative reaction takes place in the more acidic conditions generated during long

reactions.

Preliminary nmr spectra reveal that the black precipitate has a relatively simple structure, suggesting a regular repeating unit. Like its analog, polypyrrole, the oxidized imidazole appears to have no melting point. Further studies will provide conductivity values and a more complete characterization.

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